RJA 1/6/22
JS 10/21/21

INITIAL REVIEW ENGINEERING REPORT [redacted]
PMN: 18-0077

Post-Focus Draft Revision 1 7/2/2018
ENGINEER: El-Zoobi \ SL \ JAS
PV (kg/yr): [redacted] YX
Revision Notes / Assessment Overview: =====> [redacted]

SUBMITTER: Koch Agronomic Services

USE: Reagent for the controlled release of a urease inhibitor in urea-based fertilizers used on farms. %Phosphorus = 12.4% (measured). P2REC: CRSS: Forward. P2 Claim: The PMN material is intended to replace direct use of N-butyl-phosphorothioic triamide [redacted] in fertilizer formulations. NBPT, when in contact with the soil, degrades in a relatively short period of time through oxidation and hydrolysis. The PMN material is stable enough to extend the availability of NBPT, while being labile enough that NBPT is released when water is present, ensuring that a low level of NBPT is present for the days or weeks during which the urea fertilizer is taken up by the crop.

OTHER USES: All analogs [redacted]

MSDS: Yes Label: No

Gen Eqpt: Provide adequate general and local exhaust ventilation. Observe Occupational Exposure Limits and minimize the risk of inhalation of vapors and spray mist. / Wear approved safety glasses or goggles. / Chemical resistant gloves are recommended. Be aware that the liquid may penetrate the gloves. Frequent change is advisable. Suitable gloves can be recommended by the glove supplier. / Wear appropriate clothing to prevent repeated or prolonged skin contact.

Respirator: If engineering controls do not maintain airborne concentrations below recommended exposure limits (where applicable) or to an acceptable level (in countries where exposure limits have not been established), an approved respirator must be worn. Wear air supplied respiratory protection if exposure concentrations are unknown. In case of inadequate ventilation or risk of inhalation of mist, use suitable respiratory equipment with particle filter. In the United States of America, if respirators are used, a program should be instituted to assure compliance with OSHA 29 CFR 1910.134 and ANSI Z88.2.

Health Effects: Causes skin irritation. / Causes serious eye damage. / May cause respiratory irritation. / May damage fertility or the unborn child.

TLV/PEL:

[redacted]

CRSS :

Chemical Name: Urea, reaction products with N-butylphosphorothioic triamide and formaldehyde

S-H20: 0.035 g/L @
VP: 3.0E-6 torr @
MW: 239.00 %<500 %<1000
Physical State and Misc CRSS Info:

Neat: Solid Mfg: Solution, [redacted] PMN material with excess feedstocks and water of reaction Proc/Form: Solution, [redacted] PMN material End Use: Solid, PMN material coated onto granular urea fertilizer which is then applied to fields. The structures drawn are representative. The submitter provided that the PMN material consists predominantly [redacted] In addition, the submitter provided an LC-MS output which included relative percents of different components: 30.2% residual feedstock NBPT (mass 167), 41.1% undefined and inseparable components, two peaks representing mass 239 (top 2 left structures) for 4.2% and 17.5%, three peaks representing mass 311 (right 3 structures for 1.9%, 3.1%, 0.4%), and two peaks representing mass 383 (structure unclear) for 0.5% and 0.2%. Continued on page 6 of this report.

Consumer Use: No

SAT (concerns) (01/05/2018):

Related Cases and Misc SAT Info:

Analogs: [redacted]
Migration to groundwater:

PBT rating: P1B1T2
Health: 2 Dermal, Drinking Water, Inhalation, XB Testing (Testing desired)

Eco: 1 No releases to water, XB Testing (Testing desired)

OCCUPATIONAL EXPOSURE RATING: [redacted]

NOTES & KEY ASSUMPTIONS:
Occupational exposure and environmental releases were estimated using the 9/30/2013 version of ChemSTEER tool. Input to ChemSTEER tool includes information from: the PMN submission, physical / chemical properties and relevant past cases. The PMN is for use as a fertilizer. The SAT report lists concerns for inhalation, dermal, and drinking water. No releases to water. This is a health and eco exposure-based case (testing desired); therefore, a full assessment was performed. Note: fertilizer application to farm sites is expected to result in 100% land release. The following past fertilizer cases are referenced for consistency (all different submitters, similar use): [redacted] /// USE: All past cases assumed [redacted] applications/site (consistent with this IRER). All past cases assessed 100% release scenarios from farm application (consistent with this IRER). [redacted] were solids and assessed inhalation exposure (not consistent with this IRER; this IRER was coated onto solids with avg. diameter of 2mm for which dust generation is not expected. Additionally, the coated PMN solution is expected to suppress dust generation). [redacted] is a liquid. All past cases assessed exposures to 3 workers/site (consistent with this IRER).

POLLUTION PREVENTION CONSIDERATIONS:

P2 Claim: K32 is a product specifically designed to provide an agricultural benefit to farmers while reducing the ecological impact of surface applied urea-containing products. The agronomic benefit of using urease inhibitors is well-documented in the peer-reviewed literature. One of the benefits to farmers of urease inhibitors is the achievement of a higher production yield per acre. If growers practice proper nutrient management, farmers are expected to benefit from a reduced amount of nutrient inputs needed for an equivalent yield compared to conventional fertilizer applications. In many cases, with proper nutrient management, farmers are expected to experience a combination of both higher yield and lower nutrient inputs. K32 is a novel urease inhibitor that reduces the environmental impact caused by the use of agricultural fertilizers without introducing additional risks from adjuvants. K32 reduces ammonia emissions that typically occur after surface application of urea-containing fertilizers. This emission loss negatively affects crop productivity and profitability of a farming enterprise and it contributes to air and water pollution. Ammonia gas from agricultural activities combines with other atmospheric components to form air particulates which are partially responsible for reduced visibility and possible breathing difficulties. Ammonia emissions also contribute to the redistribution of nitrogen in the environment; the ammonia may be re-deposited on ecologically sensitive tracts that are spatially separated from the original application area or deposited in surface waters where the ammonia can contribute to eutrophication. Urease inhibitors are important tools in the effort to reduce nutrient loss and preserve air and water quality. The American Association of Plant Control Officials (AAPFCO) currently defines urease inhibitors as substances which inhibit hydrolytic action on urea by the enzyme urease. When applied to soil surfaces, urea rapidly begins to hydrolyze due to the action of naturally occurring urease, a ubiquitous enzyme present in all soils. The products of this hydrolysis are ammonia and carbon dioxide (CO2), which are rapidly lost to the environment through air emissions. Nitrogen losses in such situations are typically 20-30% but may reach excesses of 70% (Kiss and Simihaian 2002). AAPFCO also defines any fertilizer that contains a urease inhibitor as an Enhanced Efficiency Fertilizer (EEF). EEFs are fertilizer products with characteristics that allow increased nutrient availability and reduce potential nutrient losses to the environment (e.g., gaseous losses, leaching or runoff when compared to an appropriate reference product). EEFs are used as alternatives or complements to conventional fertilizers for their numerous agronomic, economic and environmental benefits (Thapa et al., 2016). The primary commercial urease inhibitor is N-(n-butyl

thiophosphoric triamide (NBPT). NBPT has been available prior to 1992 and is marketed by the applicant under the AGROTAIN® trade name. NBPT is added to urea- fertilizers at about 0.065% and is quite effective at reducing urea hydrolysis. Unfortunately, NBPT is effective for a relatively short period of time. Once it is in contact with the soil it degrades through oxidation and hydrolysis (Engel 2015). If there a significant time lapse between fertilizer application and rainfall, NBPT may no longer be effective because of its degradation and half-life. As a result, NBPT may not be present when the urea is subject to hydrolysis by urease (a process that requires water). Improved Urease Inhibition To improve upon the efficiency of NBPT, Koch Agronomic Services researched ways to prolong the half-life, to ensure that NBPT is present in the soil when needed, to prevent the hydrolysis of urea. KAS discovered that it could combine NBPT with formaldehyde and urea in a reaction product mixture. The resultant adducts, typically adducts between formaldehyde and 1 or 2 equivalents of NBPT and urea, are the ingredients of K32 that provide urease inhibition. The K32 adducts are stable enough to extend the availability of NBPT, while being labile enough that NBPT is released when water is present, ensuring that a low level of NBPT is present for the days or weeks during which the urea fertilizer is taken up by the crop. K32 is a significant improvement over NBPT and other urease inhibitors currently on the market. Using K32 in place of NBPT broadens the array of fertilizers that qualify as EEFs and can play a part in reducing impacts to air and water that result from the enzymatic hydrolysis of urea. Laboratory and field trials using K32 have repeatedly shown the potential to increase yield and to preserve nutrients by inhibiting the degradation of urea and the associated volatilization of ammonia. K32 outperforms the current urease inhibitor products on the market. Particularly in acidic soils, K32 demonstrates benefits above those of NBPT alone, as NBPT is particularly susceptible to abiotic chemical degradation and mineralization in acidic soils. Environmental Performance and Potential By reducing the amount of urea converted to ammonia, K32 significantly reduces the amount of nitrogen needed to achieve the intended agronomic benefit and reduces ammonia releases to air (and water via re-deposition). As shown in Table 1 & 2, research work with multiple university programs has demonstrated that the addition of K32 results in measurable yield increases or improvement in ammonia volatilization. The current estimated amount of urease-inhibitor-treated urea in the United States is 2-3 million tons. Roughly, 800,000 tons of that material has the potential to be lost as ammonia from volatilization. If farmers increase efficiencies through the use of K32, they may be able to recoup 60% of the lost nitrogen, potentially saving 480,000 tons of fertilizer that would

otherwise be lost to the environment and potentially impact the quality of air and surface waters. [See attachment 24_K32 Environmental Benefit submission 3 dt.pdf to the submission] P2REC: CRSS: Forward.

EXPOSURE-BASED REVIEW: [redacted] [redacted]

1) # of workers exposed: [redacted] >1000? [redacted]

2) >100 workers with >10 mg/day inhalation exposure: [redacted]

3) (a) >100 workers w/1-10 mg/day inh. exp. & >100 days/yr: [redacted]

   (b) Routine Dermal Cont: >250 workers & >100 days/yr: [redacted]

INITIAL REVIEW ENGINEERING REPORT [redacted]

PMN: 18-0077

Manufacturing: Batch

Number of Sites/ Location: [redacted]

[redacted]

Days/yr: [redacted]

Basis: Submission specifies [redacted] kg/bt, [redacted] hr/bt, [redacted] bt/yr, and [redacted] PMN in product.

Process Description: [redacted]

ENVIRONMENTAL RELEASES ESTIMATE SUMMARY

IRER Note: The daily releases listed for any source below may coincide with daily releases from the other sources to the same medium.

Air
Output 2: [redacted] kg/site-day over [redacted] days/yr from [redacted]
or [redacted] kg/site-yr from [redacted] or [redacted] kg/yr-all sites
to: Air (submission)
from: Loading Liquid Product into Drums
basis: User-Defined Loss Rate Model. The submitter estimates [redacted] kg/bt released as fugitive air during container loading.

Air
Output 2: [redacted] kg/site-day over [redacted] days/yr from [redacted]
or [redacted] kg/site-yr from [redacted] or [redacted] kg/yr-all sites
to: Air (submission)
from: Sampling Liquid Product
basis: User-Defined Loss Rate Model. The submitter estimates [redacted] kg/bt released as fugitive air during sampling.

Incineration
Output 2: [redacted] kg/site-day over [redacted] days/yr from [redacted]
or [redacted] kg/site-yr from [redacted] or [redacted] kg/yr-all sites
to: Off-site incineration (submission)
from: Equipment Cleaning Losses of Liquids from a Single, Large Vessel

basis: User-Defined Loss Rate Model. Submitter states: [redacted] The submitter estimates [redacted] kg/bt ([redacted]) is released to off-site incineration from equipment cleaning.

RELEASE TOTAL
[redacted] kg/yr - all sites

OCCUPATIONAL EXPOSURES ESTIMATE SUMMARY
Tot. # of workers exposed via assessed routes: 6
Basis: Submission estimates up to 6 workers exposed. RAD assumes each worker may be exposed at the highest potential exposures for each physical form, as conservative.

Inhalation:

negligible, VP < 0.001 torr and generation of respirable PMN not expected during MFG.

Dermal:

Exposure to Liquid at [redacted] concentration
High End:
> Potential Dose Rate: [redacted] mg/day over [redacted] days/yr
> Lifetime Average Daily Dose: [redacted] mg/day over [redacted] days/yr
> Average Daily Dose: [redacted] mg/day over [redacted] days/yr
> Acute Potential Dose: [redacted] mg/day over [redacted] days/yr
Number of workers (all sites) with dermal exposure: 6
Basis: Loading Liquid Product into Drums; EPA/OPPT 2-Hand Dermal Contact with Liquids Model. Per November 2016 RAD guidance, default parameters for this model were updated: body weight (BW) was updated from 70 to 80 kg and Averaging Time over a Lifetime (ATc) was updated from 70 to 78 years.

INITIAL REVIEW ENGINEERING REPORT [redacted]

PMN: 18-0077

Processing: Fertilizer Formulation

Number of Sites/ Location: 500

unknown site(s)

Days/yr: 30

Basis: Submission estimates 500 sites and 30 exposure days (RAD assumes exposure days are equal to operating days). CS calculates 40 kg PMN/site-day.

Process Description: PMN received (liquid, [redacted]) --> charged to horizontal rotating blender with urea --> mix until evenly distributed (PMN solution coats urea fertilizer granule) --> convey matreial to transport vessel or tractor spreader (solid, [redacted]) (submission and subsequent information from the submitter)

ENVIRONMENTAL RELEASES ESTIMATE SUMMARY

IRER Note: The daily releases listed for any source below may coincide with daily releases from the other sources to the same medium. Submission indicates PMN solution is coated onto urea fertilizer granules with an average diameter of 2mm. Dust generation is not expected for particles >250 microns. Additionally, the submission indicates the PMN solution is expected to suppress dust generation during blending. Therefore, RAD did not assess release from fugitive dust emissions.

Water
High End: [redacted]kg/site-day over 14 days/yr from 500 sites
or [redacted] kg/site-yr from 500 sites or [redacted] kg/yr-all sites
to: On-site wastewater treatment (submission)
from: Cleaning Liquid Residuals from Drums Used to Transport the Raw Material
basis: EPA/OPPT Drum Residual Model, CEB standard 3% residual. Submission estimates [redacted] kg PMN/site-day released to on-site WWT from container cleaning. RAD standard model is more conservative. Due to multiple unknown sites, RAD assesses using standard model to on-site WWT.

Water
Output 2: [redacted] kg/site-day over 30 days/yr from 500 sites
or [redacted] kg/site-yr from 500 sites or [redacted] kg/yr-all sites
to:
from: Equipment Cleaning Losses of Solids from Process Vessels
basis: EPA/OPPT Solid Residuals in Transport Containers Model, CEB standard 1% residual. Submission does not describe equipment cleaning procedures. RAD assumes equipment cleaninng wastes disposed in similar manner as container cleaning wastes. Therefore, RAD assesses 1% (standard) to on-site WWT.

Air
Output 2: [redacted] kg/site-day over 14 days/yr from 500 sites
or [redacted] kg/site-yr from 500 sites or [redacted] kg/yr-all sites
to: Air (submission)
from: Unloading Liquid Raw Material from Drums
basis: User-Defined Loss Rate Model. The submitter estimates [redacted] kg/bt released as fugitive air during container unloading.

RELEASE TOTAL
[redacted] kg/yr - all sites

OCCUPATIONAL EXPOSURES ESTIMATE SUMMARY
Tot. # of workers exposed via assessed routes: 3,000
Basis: Submission estimates 1 worker/site. RAD assesses a default minimum of 3 workers/site.

Inhalation:

Negligible for liquids, VP <0.001 torr and generation of respirable PMN not expected from PROC. // Submission indicates PMN solution is coated onto urea fertilizer granules with an average diameter of 2mm. Dust generation is not expected for particles >250 microns. Additionally, the submission indicates the PMN solution is expected to suppress dust generation during blending. Therefore, RAD did not assess inhalation exposure to fugitive dust emissions.

Dermal:

Submission indicates the solid product material then conveyed from the blending tank to the application vehicle. The mixing and conveying systems are remotely controlled and the operators are not directly exposed to the treated material. Due to unknown sites, RAD conservatively assesses dermal exposures to solids during loading.

Exposure to Liquid at [redacted] concentration

High End:

> Potential Dose Rate: [redacted] mg/day over 30 days/yr

> Lifetime Average Daily Dose: [redacted] mg/day over 30 days/yr

> Average Daily Dose: [redacted] mg/day over 30 days/yr

> Acute Potential Dose: [redacted] mg/day over 30 days/yr

Number of workers (all sites) with dermal exposure: 1,500

Basis: Unloading Liquid Raw Material from Drums; EPA/OPPT 2-Hand Dermal Contact with Liquids Model. Per November 2016 RAD guidance, default parameters for this model were updated: body weight (BW) was updated from 70 to 80 kg and Averaging Time over a Lifetime (ATc) was updated from 70 to 78 years.

Exposure to Solid at [redacted] concentration

High End:

> Potential Dose Rate: [redacted] mg/day over 30 days/yr

> Lifetime Average Daily Dose: [redacted] mg/day over 30 days/yr

> Average Daily Dose: [redacted] mg/day over 30 days/yr

> Acute Potential Dose: [redacted] mg/day over 30 days/yr

Number of workers (all sites) with dermal exposure: 1,500

Basis: Loading Solid Product into Transport Containers; EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model. Per November 2016 RAD guidance, default parameters for this model were updated: body weight (BW) was updated from 70 to 80 kg and Averaging Time over a Lifetime (ATc) was updated from 70 to 78 years.

INITIAL REVIEW ENGINEERING REPORT [redacted]

PMN: 18-0077

Use: Fertilizer Application

Number of Sites/ Location: 5,000

unknown site(s)

Days/yr: 4

Basis: Past cases assume 4 fertilizer applications/site-yr. Updated information from the submitter indicated that there would be on the order of 5,000 sites. At 5,000 sites and 4 applications, CS calculates [redacted] kg PMN/site-day.

Process Description: Tractor/ trucks containing PMN treated granular urea (solid, <[redacted]) arrive at agricultural fields --> treated urea spread on agricultural fields (submission and subsequent information provided by submitter)

ENVIRONMENTAL RELEASES ESTIMATE SUMMARY

IRER Note: The daily releases listed for any source below may coincide with daily releases from the other sources to the same medium. Submission indicates PMN solution is coated onto urea fertilizer granules with an average diameter of 2mm. Dust generation is not expected for particles >250 microns. Additionally, the submission indicates the PMN solution is expected to suppress dust generation. Therefore, RAD did not assess release from fugitive dust emissions.

Water or Incineration or Landfill
Output 2: [redacted] kg/site-day over 4 days/yr from 5,000 sites
or [redacted] kg/site-yr from 5,000 sites or [redacted] kg/yr-all sites
to: Uncertain
from: Cleaning Solid/ Powder Residuals from Containers Used to Transport the Raw Material
basis: EPA/OPPT Solid Residuals in Transport Containers Model, CEB standard 1% residual. Submission does not address container cleaning during use. RAD assesses per standard model to uncertain media.

Other
Output 2: [redacted] kg/site-day over 4 days/yr from 5,000 sites
or [redacted] kg/site-yr from 5,000 sites or [redacted] kg/yr-all sites
to: Farmland (per submission)
from: Unloading Solid Raw Material from Transport Containers
basis: User-Defined Loss Rate Model. RAD assumes a 100% release scenario as the fetilizer is applied to land (consistent with past cases). Accounting for upstream container cleaning losses, LF = [redacted]

RELEASE TOTAL
[redacted] kg/yr - all sites

OCCUPATIONAL EXPOSURES ESTIMATE SUMMARY
Tot. # of workers exposed via assessed routes: 15,000
Basis: Submission did not estimate number of workers. RAD assessed a default minimum of 3 workers/site.

Inhalation:

Submission indicates PMN solution is coated onto urea fertilizer granules with an average diameter of 2mm. Dust generation is not expected for particles >250 microns. Additionally, the submission indicates the PMN solution is expected to suppress dust generation. Therefore, RAD did not assess inhalation exposure to fugitive dust emissions.

Dermal:

Submission indicates the worker is typically isolated in the cab of the tractor or truck; therefore, the exposure level is minimal. Due to unknown sites, RAD conservatively assesses dermal exposures during unloading of containers (i.e., application of fertilizer).

Exposure to Solid at [redacted] concentration
High End:
> Potential Dose Rate: [redacted] mg/day over 4 days/yr
> Lifetime Average Daily Dose: [redacted] mg/day over 4 days/yr
> Average Daily Dose: [redacted] mg/day over 4 days/yr
> Acute Potential Dose: [redacted] mg/day over 4 days/yr
Number of workers (all sites) with dermal exposure: 15,000
Basis: Unloading Solid Raw Material from Transport Containers; EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model. Per November 2016 RAD guidance, default parameters for this model were updated: body weight (BW) was updated from 70 to 80 kg and Averaging Time over a Lifetime (ATc) was updated from 70 to 78 years.